Role of hydrogen in doping of GaN

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We investigate the interactions between hydrogen and dopant impurities in GaN, using state-of-the-art first-principles calculations. Our results for energetics and migration reveal a fundamental difference in the behavior of hydrogen between p-type and n-type material; in particular, we explain why hydrogen concentrations in n-type GaN are low, and why hydrogen has a beneficial effect on acceptor incorporation in p-type GaN. Our results identify the conditions under which hydrogen can be used to control doping in semiconductors in general. © 1996 American Institute of Physics. [S0003-6951(96)02713-2]

Despite the successful application of GaN in the fabrication of highly efficient blue light emitting diodes (LEDs), doping problems remain an important issue. As-grown GaN is typically n-type conductive, and p-type doping levels are still limited. For GaN grown by MOCVD (metal-organic chemical vapor deposition) and doped with Mg, Amano et al. showed that p-type conductivity can be achieved by activating the Mg acceptors using low-energy electron-beam irradiation (LEEBl). Nakamura et al. subsequently demonstrated that the activation of Mg acceptors can also be achieved by thermal annealing, and that this process can be reversed by annealing in a hydrogen ambient, revealing the crucial role played by hydrogen. Based on these observations Van Vechten et al. suggested that hydrogen enables p-type doping by suppressing compensation by native defects. These authors went on to propose the incorporation (and subsequent removal) of hydrogen as a general method for improving p-type as well as n-type doping of wide-band-gap semiconductors. The Van Vechten model highlights the important role of hydrogen, but leaves various issues unexplained, such as the lack of hydrogen incorporation in n-type GaN, and the success of p-type doping (without post-growth treatments) in MBE (molecular-beam epitaxy).

In this letter we address the fundamental mechanisms governing the interaction of hydrogen with dopants in GaN. We have recently investigated energetics and migration of monatomic hydrogen and hydrogen around a Mg acceptor using state-of-the-art first-principles calculations, finding that H acts as a donor (H\(^+\)) in p-type GaN, and as an acceptor (H\(^-\)) in n-type material. Here we combine these results with our detailed investigations of native defects in GaN\(^-\) to elucidate the role of hydrogen in doping and compensation of GaN. More generally, we will identify conditions under which hydrogen is beneficial for doping, and discuss the limitations of this process. For n-type material, we explain why little or no hydrogen incorporation occurs. For p-type GaN doped with Mg, we find that hydrogen enhances the solubility of the acceptor species, and suppresses native defect compensation. We also address the mechanism of the post-growth Mg activation.

The equilibrium concentration \(c\) of an impurity or defect at temperature \(T\) is determined by its formation energy, \(E^f\):

\[
\begin{align*}
\frac{c}{N_{\text{sites}}} &= e^{-E^f/k_B T}, \\
E^f &= E^\text{tot}(\text{GaN:Mg}) - E^\text{tot}(\text{GaN-bulk}) - \mu_{\text{Mg}} q E_F - \mu_{\text{Ga}} - q E_F,
\end{align*}
\]

where \(N_{\text{sites}}\) is the number of sites where the defect can be formed, and \(k_B\) the Boltzmann constant. The formation energy depends on various parameters. For example, the formation energy of a Mg acceptor is determined by the relative abundance of Mg, Ga, and N atoms. In a thermodynamic context these abundances are described by the chemical potentials \(\mu_{\text{Mg}}\), \(\mu_{\text{Ga}}\), and \(\mu_{\text{N}}\). If the Mg acceptor is charged, the formation energy depends further on the Fermi level \((E_F)\), which acts as a reservoir for electrons. Forming a substitutional Mg acceptor requires the removal of one Ga atom and the addition of one Mg atom; the formation energy is therefore:

\[
E^f(\text{GaN: Mg}) = E^\text{tot}(\text{GaN:Mg}) - E^\text{tot}(\text{GaN-bulk}) - \mu_{\text{Mg}} + \mu_{\text{Ga}} + q E_F,
\]

where \(E^\text{tot}(\text{GaN:Mg})\) is the total energy derived from a calculation for substitutional Mg, \(E^\text{tot}(\text{GaN-bulk})\) is the total energy of the corresponding GaN bulk supercell, and \(q\) is the charge state of the Mg acceptor. Similar expressions apply to the hydrogen impurity, and to the various native defects. Details about the first-principles calculations and convergence checks have been published elsewhere. Error bars on the formation energies and defect levels due to supercell effects and entropy contributions are on the order of a few tenths of an eV. These error bars are small enough not to affect any qualitative conclusions.

For the following discussion we consider Ga-rich conditions \((\mu_{\text{Ga}} > \mu_{\text{Ga bulk}})\) which are common for GaN growth. We further take into account that the Mg concentration is limited by the formation of Mg\(_3\)N\(_2\) \((\mu_{\text{Mg}} = \mu_{\text{Mg}} N_2)\), which produces a lower limit for the formation energy, and an upper limit for the Mg concentration (solubility limit). By fixing the chemical potentials the formation energy becomes solely a function of the Fermi energy [see Eq. (2)]. This relation is shown in Fig. 1(a), which also includes the formation energy of the hydrogen species, as well as the dominant native defect; under p-type conditions this defect is the nitrogen vacancy \((V_N)^-\).

The slope of the formation energies characterizes the charge state: a positive slope (as observed for \(V_N^-\)) indicates a positive charge state, corresponding to a donor. For Mg,
In a plot such as Fig. 1(a), the equilibrium Fermi level position can be estimated to be near the crossing point between the acceptor and the dominant donor species. At this point their formation energies, and hence their concentrations, are equal, ensuring charge neutrality – at least if we ignore free carriers, a reasonable approximation if the Fermi level is far enough from the valence-band edge. If only Mg acceptors and native defects are present, the crossing occurs at a Fermi energy \( E_F = 0.8 \text{ eV} \). If additionally H is present, the crossing point shifts to higher energies. As can be seen in Fig. 1(a) an increase in the Fermi level decreases the formation energy for the Mg acceptor and increases the formation energy for \( V_N \), thus resulting in a lowered defect concentration and an increased acceptor incorporation. Both phenomena are directly related to the abundance of hydrogen in the sample; in our discussion, we assumed \( \mu_H = \mu_{H^+} \). One could consider making the environment even more hydrogen-rich, for instance by introducing atomic hydrogen (from a plasma).

We thus find that Mg-doped GaN grown at high temperatures (above 1200 K) will always be heavily compensated: the compensating centers are either N vacancies or hydrogen, if present. This conclusion is consistent with experimental observations: the only cases where \( p \)-type GaN has been achieved without any post-growth treatments involved MBE growth, which is characterized by lower growth temperatures (below 1000 K) and the absence of H.\(^9,10\) When H is present, the H concentration essentially equals the Mg concentration [see Fig. 1(c)]. The H donors and Mg acceptors can actually form electrically neutral complexes, with a binding energy of 0.7 eV.\(^4\) For the specific choice of chemical potentials made here, this binding energy is low enough for the complexes to be dissociated at the growth temperature; however, the Mg and H will form pairs when the sample is cooled to room temperature, consistent with experimental observations.\(^11\)

In order to activate the Mg, post-growth treatments are necessary. The first step in the activation process is the dissociation of the Mg-H complex. Our estimated dissociation barrier for the complex is 1.5 eV, calculated by considering a jump to a nearest-neighbor site; the total barrier may be slightly higher.\(^4\) This barrier should be low enough to be overcome at modest annealing temperatures (around 300 °C). It has been found, however, that thermal annealing of MOCVD-grown Mg-doped GaN needs to be carried out at much higher temperatures in order to activate the Mg.\(^2\) The reason is that mere dissociation of the Mg-H complex is insufficient; the H which is released from the Mg acceptors needs to be either removed (to the surface or into the substrate) or neutralized (e.g., at extended defects). Otherwise the H atom (a donor) continues to compensate the Mg, and is recaptured when the sample is cooled down again. The phenomenon is well known from studies of complex dissociation in Si, where annealing in the presence of an electric field (which sweeps the hydrogen out of the region) leads to acceptor activation at much lower temperatures than in the absence of a field.\(^12\)

We have calculated a diffusion barrier for \( H^+ \) of 0.7 eV\(^4\) indicating that \( H^+ \) is highly mobile. The high temperatures required for Mg activation through thermal annealing there-
fore reflect an activation barrier for incorporating hydrogen in a different form inside the $p$-doped layer (e.g., attached to extended defects), or for removal of H from the layer through desorption from the surface. Note that the annealing temperature should be kept low enough to prevent the formation of nitrogen vacancies or the diffusion of the Mg acceptors. This condition is met in GaN, judging by the success of thermal annealing procedures.\textsuperscript{2} We suggest that it is the inability to meet this requirement which causes problems with obtaining $p$-type conduction in MOCVD-grown nitrogen-doped ZnSe: the N acceptors are passivated by hydrogen during growth, and a high annealing temperature would be required to remove the hydrogen; this temperature apparently exceeds the temperatures at which good crystalline quality of ZnSe can be maintained.\textsuperscript{13} When only Si and native defects are present, Fig. 1(d) shows that the Si and the Ga-vacancy concentration (the dominant native defect under $n$-type conditions) increase with temperature. However, even at the high growth temperatures characteristic of MOCVD (about 1300 K) the concentration of Ga vacancies is orders of magnitude lower than the Si concentration, indicating that native defect compensation is not a problem.

If hydrogen is present, a fraction of the Si donors will be compensated [Fig. 1(d)]. However, even at very high growth temperatures the hydrogen concentration remains well below the Si concentration, explaining why Si remains electrically active even when H is present during growth. The Si concentration is also largely unaffected by the presence of hydrogen, unlike the Mg-doped case. We have investigated the formation of Si-H complexes, and found them to have essentially the same binding energy as Mg-H (0.7 eV); however, very few such complexes are formed because of the overall low H concentration. It is actually fortunate that hydrogen does not readily incorporate in $n$-type GaN: our calculated diffusion barrier for H\textsuperscript{+} ($\approx$ 3.4 eV), is so high as to render it immobile in $n$-type GaN, which would make it very hard to remove any hydrogen from the material (unlike the case of $p$-type GaN, in which H\textsuperscript{+} diffuses readily and can be removed by annealing).

The lack of hydrogen incorporation in $n$-type GaN is due to its significantly higher formation energy, as compared to $p$-type material [compare Figs. 1(a) and 1(b)]. This higher formation energy (and consequently lower solubility) also explains why post-growth hydrogenation of $n$-type GaN does not produce any effects\textsuperscript{11}; in addition, the high diffusion barrier of H\textsuperscript{+} makes it very difficult for hydrogen to move into $n$-type GaN.

Our conclusions support the potential use of hydrogen as a means of improving the doping in wide-band-gap semiconductors; however, this approach is by no means as generally applicable as suggested by Van Vechten \textit{et al.}.\textsuperscript{3} The following are necessary conditions to use H passivation as a tool to enhance doping: (i) H must be the dominant compensating defect (i.e., its formation energy must be lower than that of \textit{all} native defects and comparable to the formation energy of the dopant impurity), (ii) the activation barriers to dissociate the H-impurity complex and to remove or neutralize H must be lower than the activation energies for native-defect formation or the diffusion barrier of the impurity, and (iii) the dissociated H atom must be highly diffusive. We note that these conditions are not particular for GaN but apply to any semiconductor. Whether these conditions are realized, however, depends on the specific case (semiconductor, impurity, growth conditions) and must be addressed independently for each system.

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